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THERMODYNAMICS AND HIGHER-ORDER FLUID THEORIES

by D. C. Leigh

Prepared under Grant No. NsG-664 *by*
PRINCETON UNIVERSITY
Princeton, N.J.

for

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ABSTRACT

Four boundary value problems in unsteady simple shear flow are considered. Solutions for the second-order fluid approximation are listed, including a solution which seems to be new. For the third-order fluid approximation, solutions are obtained for the linearized versions of the various problems. The Second Law of Thermodynamics, reduced to the requirement that the rate of deformation work be non-negative, is applied to these solutions. The signs of the pertinent second-order material constant is not determined whereas the signs of the pertinent third-order constants are determined. On the other hand, the Second Law places restrictions on the allowable solutions; for some problems no solution is valid. The implications of these results are discussed.

Contents

1. Introduction

1.1 Simple fluids and n-th order approximations

Noll[1] has defined a general type of nonlinear fluid with memory which is called a simple fluid. In this paper we shall be concerned only with imcompressible fluids so that the constitutive equation takes the form

$$\underset{\sim}{T} = -p\underset{\sim}{I} + \underset{s=0}{\overset{\infty}{\underset{\sim}{f}}}\left(\underset{\sim}{G}(s)\right) \tag{1.1}$$

where $\underset{\sim}{T}$ is the stress tensor, p is the indeterminate pressure, $\underset{\sim}{I}$ the identity tensor, $\underset{s=0}{\overset{\infty}{\underset{\sim}{f}}}\left(\underset{\sim}{G}(s)\right)$ is a functional over the deformation history tensor $\underset{\sim}{G}$ (s). Throughout this paper we will call $\underset{\sim}{T} + p\underset{\sim}{I}$ the extra stress and denote it by $\underset{\sim}{S}$. The deformation history tensor is given by

$$\underset{\sim}{G}(s) = \underset{\sim}{C}_{(t)}(t-s) - \underset{\sim}{I} \tag{1.2}$$

where

$$\underset{\sim}{C}_{(t)}(t-s) = \underset{\sim}{F}^{T}_{(t)}(t-s)\,\underset{\sim}{F}_{(t)}(t-s) \tag{1.3}$$

and

$$\underset{\sim}{F}_{(t)}(t-s) = \frac{\partial}{\partial \underset{\sim}{x}}\underset{\sim}{\xi}(\underset{\sim}{x}, t-s) \tag{1.4}$$

where $\underset{\sim}{\xi}$ is location at time (t - s) of the material particle which is at $\underset{\sim}{x}$ at time t. In (1.1) the functional must be isotropic in $\underset{\sim}{G}$(s)

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1 W. Noll, Arch. Ratl. Mech. Anal. $\underset{\sim}{2}$, 197 (1958).

and we impose the conditions that if the fluid has been at rest for all time the extra stress is zero, that is

$$\underset{s=0}{\overset{\infty}{\mathfrak{f}}}(\underset{\sim}{0}) = \underset{\sim}{0} \tag{1.5}$$

and thus p is a hydrostatic pressure. Simple fluids include the phenomenon of stress relaxation as well as nonlinear shear stress versus shear rate, and, unequal normal stresses.

Coleman and Noll[2] have shown that if the functional $\underset{\sim}{f}$ is n-times differentiable in a suitable way with respect to the deformation history $\underset{\sim}{G}$ and if $\underset{\sim}{G}(s)$ has n derivatives at $s = 0$, the following constitutive equation is a suitable n-th order approximation for slow enough motions:

$$\underset{\sim}{T} = -p\underset{\sim}{I} + \sum_{(j_1 \dots j_k)} \underset{\sim}{\ell}_{j_1 \dots j_k}\left[\underset{\sim}{A}_{j_1} \dots \underset{\sim}{A}_{j_k}\right] \tag{1.6}$$

where the summation is over all sets of integers $j_1 \dots j_k$ for which

$$1 \leq j_1 \leq \dots \leq j_k \leq n \qquad j_1 + \dots + j_k \leq n \tag{1.7}$$

The A_i are Rivlin-Ericksen tensors which have the curvilinear-coordinate component form

$$(\underset{\sim}{A}_i)_{km} = \overset{(i)}{x}_{k,m} + \overset{(i)}{x}_{m,k} + \sum_{j=1}^{(i-1)} \binom{i}{j} \overset{(j)}{x}{}^{p}{}_{,k} \overset{(i-j)}{x}_{p,m} \tag{1.8}$$

where, for example, $\overset{(i)}{x}_{k,m}$ is the convariant derivative with respect to the position coordinate x^m of the k-th component of the i -th accelera-

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[2] B. D. Colman and W. Noll, Arch. Ratl. Mech. Anal. 6, 355 (1960).

tion. The $\underset{\sim}{\ell}_{j_1 \cdots j_k}$ are material coefficients and the relation (1.6) is linear and isotropic in each $\underset{\sim}{A}_i$.

The precise manner in which (1.6) is an approximation to (1.1) can be found in Ref. 2. Suffice it to say here that if the time scale is slowed down by a factor α, $0 \leq \alpha \leq 1$, the error made in approximating (1.1) by (1.6) is higher than order n in α. In particular (1.6) does not include stress relaxation effects; that is, if the first n time derivatives of the motion vanish the stress reduces to the hydrostatic pressure.

A logical question to ask is whether the constitutive equation (1.6) can be any more than an n-th order approximation to a simple fluid. That is, is it reasonable to assert that (1.6) could represent a fluid for all histories no matter what their magnitude; can we talk about n-th order fluids? This question will be partially answered in the remainder of this paper.

1.2 The Second Law of Thermodynamics

The differential balance of energy can be written in the form

$$\rho \dot{\varepsilon} = tr(\underset{\sim}{T}\underset{\sim}{D}) - \underset{\sim}{\nabla} \cdot \underset{\sim}{q} + \rho r \tag{1.9}$$

where $\underset{\sim}{D} = \frac{1}{2}\underset{\sim}{A}_1$ is the rate of deformation tensor, ε is the internal energy per unit mass, $\underset{\sim}{q}$ is the heat flux vector and r is the heat supply per unit mass and ρ is the density. The differential entropy balance is given by

$$\rho \dot{\eta} = -\underset{\sim}{\nabla} \cdot \frac{\underset{\sim}{q}}{\theta} + \rho \frac{r}{\theta} + \rho \gamma \tag{1.10}$$

where η is the entropy per unit mass, θ is the absolute temperature and γ is the entropy production per unit mass. Following Coleman and Noll[3]

[3] B. D. Coleman and W. Noll, Arch. Ratl. Mech. Anal., 13, 167 (1963).

we state the Second Law of Thermodynamics as the requirement that γ be non-negative for all admissible thermo-mechanical processes. By admissible thermo-mechanical processes are meant processes which satisfy the balance of linear momentum as well as the balance of energy and also satisfy all assumed constitutive equations. The Second Law thus is seen to place restrictions on the allowable constitutive equations and/ or, as we shall see, on the allowable motions. From (1.9) and (1.10) we get for the Second Law

$$\rho\theta\gamma = \rho(\theta\dot{\eta} - \dot{\varepsilon}) + tr(\underset{\sim}{T}\,\underset{\sim}{D}) - \frac{1}{\theta}\underset{\sim}{q}\cdot\underset{\sim}{\nabla}\theta \qquad (1.11)$$

For an incompressible material (1.11) reduces to

$$\rho\theta\gamma = \rho(\theta\dot{\eta} - \dot{\varepsilon}) + tr(\underset{\sim}{S}\,\underset{\sim}{D}) - \frac{1}{\theta}\underset{\sim}{q}\cdot\underset{\sim}{\nabla}\theta \qquad (1.12)$$

We can restrict our attention to purely mechanical variables by assuming that the entropy and internal energy are constant, and, that the entropy production due to heat conduction vanishes, so that (1.12) reduces to

$$\rho\theta\gamma = tr(\underset{\sim}{S}\,\underset{\sim}{D}) \geq 0 \qquad (1.13)$$

which says that the entropy production is due entirely to the rate of deformation work. We cannot say how much the above assumptions are restrictions until we say something about the constitutive equations for the thermal variables ε , η and $\underset{\sim}{q}$. Materials and conditions for which the inequality (1.13) holds are discussed by Coleman[4]. We will comment further on this point

[4] B. D. Coleman, Arch. Ratl. Mech. Anal., **9**, 273 (1962). The starting point of the relevant discussion in that reference is justified by B. D. Coleman, Arch. Ratl. Mech. Anal., **17**, 1 (1964) which contains a general thermodynamic theory of materials with memory.

in Section 4. Such considerations are beyond the scope of this paper. However, we can note the following. If there is no heat flow, which is the case for an adiabatic material, then by (1.9) and (1.13) we have

$$\rho r = - tr(\underset{\sim}{S}\underset{\sim}{D}) \leq 0 \tag{1.14}$$

that is, in order for the balance of energy to be maintained heat must be withdrawn at each point at a rate exactly equal to that determined by the rate of deformation work. On the other hand, if the entropy production due to heat conduction vanishes because the fluid is such a good conductor that $\underset{\sim}{\nabla}\theta$ is zero, then by (1.9), if $r = o$, we require that

$$\underset{\sim}{\nabla}\cdot\underset{\sim}{q} = tr(\underset{\sim}{S}\underset{\sim}{D}) \tag{1.15}$$

that is, $\underset{\sim}{q}$ is determined by the rate of deformation work. (Note that in the latter case $\underset{\sim}{q}$ is indeterminate in the sense that it is not determined from a constitutive equation. The situation is quite analogous to the indeterminate pressure in incompressible fluids).

1.3 Unsteady simple shear flows: boundary value problems

An unsteady simple shear flow is a flow whose velocity field $\underset{\sim}{v}$ can be represented in a Cartesian rectilinear coordinate system by the following components

$$u = u(y,t) \qquad v = 0 \qquad w = 0 \tag{1.16}$$

The differential equation form of the balance of linear momentum can be

expressed in vector notation by

$$\underset{\sim}{T}\underset{\sim}{\nabla} + \rho\underset{\sim}{b} = \rho\dot{\underset{\sim}{v}} \tag{1.17}$$

where $\underset{\sim}{\nabla}$ is the derivative operator and $\underset{\sim}{b}$ is the external body force per unit mass. We will assume that $\rho\underset{\sim}{b}$ can be derived from a potential χ by means of $\rho\underset{\sim}{b} = -\underset{\sim}{\nabla}\chi$. We then introduce in the usual way the modified pressure ϕ by means of

$$\phi = p + \chi \tag{1.18}$$

Then, in terms of the extra stress $\underset{\sim}{S}$, the balance of linear momentum becomes

$$\underset{\sim}{S}\underset{\sim}{\nabla} - \underset{\sim}{\nabla}\phi = \rho\dot{\underset{\sim}{v}} \tag{1.19}$$

Since the velocity is assumed to be independent of x and z it follows that the Rivlin-Ericksen tensors are also independent of x and z and also along with (1.16) it follows that

$$S_{xz} = S_{yz} = S_{zz} = 0 \tag{1.20}$$

It then follows that the components of (1.19) reduce to

$$\partial_y S_{xy} - \partial_x \phi = \rho\,\partial_t u \tag{1.21}$$

$$\partial_y S_{yy} - \partial_y \phi = 0 \tag{1.22}$$

$$\partial_z \phi = 0 \tag{1.23}$$

We see that the modified pressure must be independent of z and from (1.21) and (1.22) that

$$\phi = S_{yy} + x\,\psi(t) + \zeta(t) \tag{1.24}$$

and hence (1.21) reduces to

$$\partial_y S_{xy} = \rho\,\partial_t u + \psi(t) \tag{1.25}$$

where $\psi(t)$ is the modified pressure gradient in the x-direction. The analysis of this paragraph is a generalization of one contained in Markovitz and Coleman.[5]

We now list several boundary value problems in unsteady simple shear flow:

<u>Problem 1</u>: We consider the boundary conditions

$$u(0,t) = U \qquad u(L,t) = 0 \tag{1.26}$$

along with the assumption that the modified pressure ϕ has no gradient in the x - direction so that by (1.24)

$$\psi(t) = 0 \tag{1.27}$$

For arbitrary initial conditions this problem is transient as well as unsteady.

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[5] H. Markovitz and B. D. Coleman, Phys. Fluids, **7**, 833 (1964).

For this problem we make the following non-dimensionalization

$$\bar{u} = \frac{u}{U} \qquad \bar{t} = \frac{\mu t}{\rho L^2} \qquad \bar{y} = \frac{y}{L} \tag{1.28}$$

and the boundary conditions (1.26) reduce to

$$\bar{u}(0,\bar{t}) = 1 \qquad \bar{u}(1,\bar{t}) = 0 \tag{1.29}$$

The rest of the problems we consider are unsteady but oscillatory and so do not require initial conditions.

Problem 2:

$$u(0,t) = U\cos\Omega t \qquad u(L,t) = 0 \tag{1.30}$$

This time we make the following non-dimensionalization

$$\bar{u} = \frac{u}{U} \qquad \bar{t} = \Omega t \qquad \bar{y} = \frac{y}{L} \tag{1.31}$$

which reduces (1.30) to

$$\bar{u}(0,\bar{t}) = \cos\bar{t} \qquad \bar{u}(1,\bar{t}) = 0 \tag{1.32}$$

Problem 3: Consider a variation of the preceding problem in which $L = \infty$, that is we have the boundary conditions

$$u(0,t) = U\cos\Omega t \qquad u(\infty,t) = 0 \tag{1.33}$$

We introduce the non-dimensionalization

$$\bar{u} = \frac{u}{U} \qquad \bar{t} = \Omega t \qquad \bar{y} = y\sqrt{\frac{\rho\Omega}{\mu}} \tag{1.34}$$

which gives the dimensionless boundary conditions

$$\bar{u}\,(0, \bar{t}\,) = \cos \bar{t} \qquad \bar{u}\,(\infty, \bar{t}\,) = 0 \tag{1.35}$$

Problem 4: A final problem in unsteady simple shear flow has the boundary conditions

$$u(L, t) = u(-L, t) = 0 \tag{1.36}$$

with the pressure gradient in the x-direction given by

$$\psi(t) = \psi_0 + \psi_1 \cos \Omega t \tag{1.37}$$

With the non-dimensionalization

$$\bar{u} = \frac{\rho\Omega u}{\psi_0} \qquad \bar{t} = \Omega t \qquad \bar{y} = \frac{y}{L} \qquad \bar{\psi} = \frac{\psi}{\psi_0} \tag{1.38}$$

(1.36) and (1.37) reduces to

$$\bar{u}(1, \bar{t}) = \bar{u}(-1, \bar{t}) = 0 \tag{1.39}$$

and

$$\bar{\psi}(\bar{t}) = 1 + \left(\frac{\psi_1}{\psi_0}\right) \cos \bar{t} \tag{1.40}$$

2. Second-order approximation

2.1 Solutions

For $n=2$ equation (1.6) reduces to

$$\underset{\sim}{T} = -p\underset{\sim}{I} + \mu\underset{\sim}{A}_1 + \mu_1^{(2)}\underset{\sim}{A}_1^2 + \mu_2^{(2)}\underset{\sim}{A}_2 \tag{2.1}$$

where the fact has been used that for incompressible fluids $tr\underset{\sim}{A}_1 = 0$ and also all isotropic tensors have been absorbed in the indeterminate pressure term $-p\underset{\sim}{I}$. For $n=1$ we would have only the linear term $\mu\underset{\sim}{A}_1$ which comprises the classical linear theory of viscous fluids. Each of the second-order terms is nonlinear: the first because $\underset{\sim}{A}_1$ is squared and the second because $\underset{\sim}{A}_2$ contains a product term as given by (1.8). The coefficient μ is the usual linear viscosity and $\mu_1^{(2)}$ and $\mu_2^{(2)}$ are second-order material coefficients.

For unsteady simple shear flow Coleman and Noll in Ref. 2 derived the following non-zero components of the extra stress:

$$\begin{aligned} S_{xy} &= \mu u_y + \mu_2^{(2)} u_{yt} \\ S_{xx} &= \mu_1^{(2)} u_y^2 \\ S_{yy} &= (\mu_1^{(2)} + 2\mu_2^{(2)}) u_y^2 \end{aligned} \tag{2.2}$$

and from (1.25) the governing differential equation for the velocity profile:

$$\mu u_{yy} + \mu_2^{(2)} u_{yyt} = \rho u_t + \psi(t) \tag{2.3}$$

where the subscripts on u indicate partial differentiation.

It was noted by Coleman and Noll that, rather surprisingly for a nonlinear theory, the velocity profile is governed by a linear equation. However from (2.2) it is seen that the normal stresses are nonlinear as well as unequal.

We now present the solutions, for the second-order approximation theory, to the boundary value problems listed in Section 1.3.

Problem 1: Using (1.27) and (1.28) equation (2.3) reduces to

$$\bar{u}_{\bar{y}\bar{y}} + \Lambda^{(2)}\bar{u}_{\bar{y}\bar{y}\bar{t}} = \bar{u}_{\bar{t}} \tag{2.4}$$

where $\Lambda^{(2)}$ is the dimensionless group

$$\Lambda^{(2)} = \frac{\mu_2^{(2)}}{\rho L^2} \tag{2.5}$$

The steady-state solution of (2.4) is

$$\bar{u} = 1 - \bar{y} \tag{2.6}$$

and the unsteady solution which can be found by separation of variables[6], after nondimensionalizing in the above way, is

$$\bar{u} = 1 - \bar{y} + \sum_{n=1}^{\infty} A_n \exp\left[-\left(\frac{n^2\pi^2}{1+n^2\pi^2\Lambda^{(2)}}\right)\bar{t}\right]\sin n\pi\bar{y} \tag{2.7}$$

We see that a departure in the initial velocity distribution from the steady state is represented by a Fourier series. On examination of (2.7) we note that for positive $\Lambda^{(2)}$, that is for a positive value of the material constant $\mu_2^{(2)}$, every term of the series is convergent, whereas for negative $\Lambda^{(2)}$ only terms for which

$$n < \frac{1}{\pi\left|\Lambda^{(2)}\right|^{\frac{1}{2}}} \tag{2.8}$$

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6 T. W. Ting, Arch. Ratl. Mech. Anal. 14, 1 (1963)

are convergent.[7]

Problem 2: Using (1.27) and (1.31) equation (2.3) reduces to

$$\Lambda \bar{u}_{\bar{y}\bar{y}} + \Lambda^{(2)} \bar{u}_{\bar{y}\bar{y}\bar{t}} = \bar{u}_{\bar{t}} \tag{2.9}$$

We see in this case that there are two dimensionless groups: $\Lambda^{(2)}$ as given by (2.5) and Λ by

$$\Lambda = \frac{\mu}{\rho L^2 \Omega} \tag{2.10}$$

The solution, obtained by Markovitz and Coleman[8], after non-dimensionalization in the above way is

$$\bar{u} = Re\left\{\hat{u}(\bar{y})\, e^{i\bar{t}}\right\} \tag{2.11}$$

where

$$\hat{u}(\bar{y}) = \frac{\sinh m(1-\bar{y})}{\sinh m} \tag{2.12}$$

and

$$m = \left[i/(\Lambda + i\Lambda^{(2)})\right]^{\frac{1}{2}} \tag{2.13}$$

Problem 3: Using (1.27) and (1.34) equation (2.3) takes the form

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7 See also B. D. Coleman, R. J. Duffin and V. J. Mizel, "Instability and Uniqueness Theorems for the Equation $u_t = u_{xx} - u_{xtx}$ on a Strip", to appear in Arch. Ratl. Mech. Anal.

8 H. Markovitz and B. D. Coleman, Adv. Appl. Mech., Vol. 8, Academic Press, N. Y. (1964).

$$\bar{u}_{\bar{y}\bar{y}} + \Lambda^{(2)}\bar{u}_{\bar{y}\bar{y}\bar{t}} = \bar{u}_{\bar{t}} \tag{2.14}$$

where now the dimensionless group $\Lambda^{(2)}$ is given by

$$\Lambda^{(2)} = \frac{\mu_2^{(2)}\Omega}{\mu} \tag{2.15}$$

The solution to this problem was obtained by Markovitz and Coleman in Ref. 5 and, after the above non-dimensionalization, is

$$\bar{u}(\bar{y},\bar{t}) = e^{-A\bar{y}}\cos(\bar{t} - B\bar{y}) \tag{2.16}$$

where

$$A, B = \left\{ \frac{[1 + (\Lambda^{(2)})^2]^{\frac{1}{2}} \pm \Lambda^{(2)}}{2[1 + (\Lambda^{(2)})^2]} \right\}^{\frac{1}{2}} \tag{2.17}$$

The parameters A and B are always real and positive regardless of the sign or magnitude of $\Lambda^{(2)}$.

<u>Problem 4:</u> Using (1.38) equation (2.3) reduces to

$$\Lambda\bar{u}_{\bar{y}\bar{y}} + \Lambda^{(2)}\bar{u}_{\bar{y}\bar{y}\bar{t}} = \bar{u}_{\bar{t}} + 1 + \left(\frac{\psi_1}{\psi_0}\right)\cos\bar{t} \tag{2.18}$$

where Λ is given by (2.10) and $\Lambda^{(2)}$ by (2.5). The non-transient solution to this problem can be found by assuming a solution of the form

$$\bar{u}(\bar{y},\bar{t}) = \hat{u}_0(\bar{y}) + \mathcal{Re}\left\{\hat{u}_1(\bar{y})\, e^{i\bar{t}}\right\} \tag{2.19}$$

One then finds that the solution is given by

$$\hat{u}_0(\bar{y}) = \frac{1}{2\Lambda}(\bar{y}^2 - 1) \tag{2.20}$$

$$\hat{u}_1(\bar{y}) = i\left(\frac{\psi_1}{\psi_0}\right)\left[1 - \frac{\cosh m\bar{y}}{\cosh m}\right] \tag{2.21}$$

where m is given by (2.13).

2.2 Application of the Second Law

Substituting the constitutive equation (2.1) of the second-order approximation into the Second Law inequality (1.13) we find that

$$\rho\theta\gamma = \mu \, tr\, \underset{\sim}{A}_1^2 + \mu_1^{(2)} tr\, \underset{\sim}{A}_1^3 + \mu_2^{(2)} tr\,(\underset{\sim}{A}_1 \underset{\sim}{A}_2) \geq 0 \tag{2.22}$$

A solution to Sec. 2.1 which satisfies the thermal assumptions leading (1.13) must also satisfy the inequality (2.22).

For unsteady simple shear (2.22) reduces to

$$\rho\theta\gamma = 2\mu u_y^2 + \mu_2^{(2)} \frac{\partial u_y^2}{\partial t} \geq 0 \tag{2.23}$$

We see from (2.23) that for steady motion

$$\mu \geq 0 \tag{2.24}$$

which is the well-known result that the viscosity of the classical linear theory must be positive.

Consider a flow in which the velocity gradient $u_y = 0$ at some instant of time t for some y. Then u_y^2 is a minimum at that instant and

$\partial u_y^2/\partial t = 0$ and by (2.23) $\rho\theta\gamma = 0$ at such an instant. But also by (2.23) $\rho\theta\gamma$ must be a minimum when $\rho\theta\gamma = 0$ so that $\partial(\rho\theta\gamma)/\partial t = 0$, that is

$$\mu_2^{(2)} \frac{\partial^2}{\partial t^2}(u_y^2) = 0 \tag{2.25}$$

There are two possibilities: $\mu_2^{(2)} = 0$, or, $\partial^2(u_y^2)/\partial t^2 = 0$ which is equivalent to $\partial u_y/\partial t = 0$. Now assuming that $\mu_2^{(2)}$ is unequal to zero in order that we are dealing with the second-order approximational rather than the linear approximation, we have the conclusion that a flow for which $u_y = 0$ and $\partial u_y/\partial t \neq 0$ violates the Second Law of Thermodynamics in the form (1.13). In the light of this remark we now examine the four solutions for unsteady simple shear flow contained in Section 2.1.

Problem 1 : The velocity gradient calculated from (2.7) is

$$\bar{u}_{\bar{y}} = -1 + \sum_{n=1}^{\infty} n\pi A_n \exp\left[-\left(\frac{n^2\pi^2}{1+n^2\pi^2\Lambda^{(2)}}\right)\bar{t}\right]\cos n\pi\bar{y} \tag{2.26}$$

Let us suppose that there is a $\bar{y}_0$ at a certain instant of time $\bar{t}_0$ such that

$$\bar{u}_{\bar{y}}(\bar{y}_0, \bar{t}_0) = 0 = -1 + \sum_{n=1}^{\infty} B_n \tag{2.27}$$

where

$$B_n = n\pi A_n \exp\left[-\left(\frac{n^2\pi^2}{1+n^2\pi^2\Lambda^{(2)}}\right)\bar{t}_0\right]\cos n\pi\bar{y}_0 \tag{2.28}$$

that is, the velocity profile has a maximum or minimum at a certain instant

of time. Now also at $\bar{y}_o$ and $\bar{t}_o$ we have

$$\left.\frac{\partial \bar{u}_{\bar{y}}}{\partial \bar{t}}\right|_{\substack{\bar{y}=\bar{y}_o \\ \bar{t}=\bar{t}_o}} = -\sum_{n=1}^{\infty}\left(\frac{n^2\pi^2}{1+n^2\pi^2\Lambda^{(2)}}\right)B_n \tag{2.29}$$

It can be shown that if (2.27) holds then (2.29) does not vanish. Thus, for this problem flows for which the velocity gradient vanishes are not allowed. It is clear that if $\Lambda^{(2)}$ is positive and the initial profile is monotomic then zero velocity gradients will never develop. On the other, it is clear that if $\Lambda^{(2)}$ is negative and terms for which (2.8) is violated are admitted, then such terms will ultimately lead to zero velocity gradients. Therefore we conclude that for negative $\Lambda^{(2)}$, terms for which (2.8) is violated not only give rise to divergent flows but also violate the Second Law of Thermodynamics.

More information about restrictions on the motion can be found by applying the Second Law to a flow for which the summation in (2.7) contains only one term, that is

$$\bar{u} = 1-\bar{y} + A_n \exp\left[-\left(\frac{n^2\pi^2}{1+n^2\pi^2\Lambda^{(2)}}\right)\bar{t}\right]\sin n\pi\bar{y} \tag{2.30}$$

Substituting in the appropriate dimensionless form of (2.23) we get

$$(1-b)a^2 + (2-b)a + 1 \geq 0 \tag{2.31}$$

where

$$a = n\pi A_n \exp\left[-\left(\frac{n^2\pi^2}{1+n^2\pi^2\Lambda^{(2)}}\right)\bar{t}\right]\cos n\pi\bar{y} \tag{2.32}$$

$$b = \frac{n^2\pi^2\Lambda^{(2)}}{1+n^2\pi^2\Lambda^{(2)}} \tag{2.33}$$

Now the left-hand side of (2.31) is a quadratic form in a and it has the discriminant b^2 which is positive or zero. For $b \neq 0$ then the inequality is violated for some values of a whereas for b = 0, that is $\Lambda^{(2)} = 0$, the inequality is satisfied. The question then is: for a given $\Lambda^{(2)}$, for what values of n and A_n is the inequality satisfied for all $\bar{y}$? For $\Lambda^{(2)}$ positive we have

$$0 < b < 1 \qquad \text{for} \quad \Lambda^{(2)} > 0 \tag{2.34}$$

which means that the entropy production is negative when a lies in the range

$$-\frac{1}{1-b} < a < -1 \tag{2.35}$$

that is

$$-\left(1 + n^2\pi^2\Lambda^{(2)}\right) < a < -1 \tag{2.36}$$

From (2.32) and (2.36) we see that for

$$n\pi \left| A_n \right| \leq 1 \tag{2.37}$$

a does not enter the range of (2.36). Another way of stating (2.37) is that

$$-2 \leq \bar{u}_{\bar{y}} \leq 0 \tag{2.38}$$

Next let us consider negative $\Lambda^{(2)}$. We then write b in the form

$$b = \frac{-n^2\pi^2|\Lambda^{(2)}|}{1 - n^2\pi^2|\Lambda^{(1)}|} \tag{2.39}$$

Now for n restricted by (2.8) b is negative and hence (1-b) is positive so that again the entropy production is again negative over a finite range of a, this time

$$-1 < a < -(1 - n^2\pi^2|\Lambda^{(2)}|) \tag{2.40}$$

From (2.32) and (2.40) we see we must have the condition

$$n\pi|A_n| \leq 1 - n^2\pi^2|\Lambda^{(2)}| \tag{2.41}$$

which is a more severe restriction than (2.38). This can also be put in the form

$$-2 + n^2\pi^2|\Lambda^{(2)}| < \bar{u}_{\bar{y}} < -n^2\pi^2|\Lambda^{(1)}| \tag{2.42}$$

<u>Problem 2:</u> From (2.11) we have

$$\bar{u}_{\bar{y}} = Re\{\hat{u}_{\bar{y}}e^{i\bar{t}}\} \tag{2.43}$$

where from (2.12)

$$\hat{u}_{\bar{y}} = -\frac{m\cosh m(1-\bar{y})}{\sinh m} \tag{2.44}$$

Recalling that m as given by (2.13) is complex we see that there are many possibilities for $\bar{u}_{\bar{y}}$ to be zero. It is clear from the boundary conditions of the problem that for a given $\bar{y}$ the velocity gradient is periodic with the same frequency as the oscillating wall. Now from (2.43) we have

$$\frac{\partial \bar{u}_{\bar{y}}}{\partial \bar{t}} = \mathcal{R}e\left\{ i\, \hat{u}_{\bar{y}}\, e^{i\bar{t}} \right\} \tag{2.45}$$

Now let $\hat{u}_{\bar{y}} = re^{i\phi}$ and therefore

$$\bar{u}_{\bar{y}} = \mathcal{R}e\left\{ re^{i\phi} e^{i\bar{t}} \right\} = r\cos(\phi + \bar{t}) \tag{2.46}$$

When $\bar{u}_{\bar{y}} = 0$ we have $(\phi + \bar{t}) = \pi/2$ modulo π. Now

$$\frac{\partial \bar{u}_{\bar{y}}}{\partial \bar{t}} = \mathcal{R}e\left\{ ire^{i\phi} e^{i\bar{t}} \right\} = r\cos\left(\phi + \bar{t} + \frac{\pi}{2}\right) \tag{2.47}$$

which is not zero when $(\phi + \bar{t}) = \pi/2$ modulo π. Therefore this problem violates the Second Law for all values of the parameters of the problem.

<u>Problem 3:</u> From the solution (2.16) and (2.17) we get that the velocity gradient vanishes for all $(\bar{y}_0, \bar{t}_0)$ which satisfy

$$\tan(\bar{t}_0 - B y_0) = \frac{A}{B} \tag{2.48}$$

For such $(\bar{y}_0, \bar{t}_0)$

$$\frac{\partial \bar{u}_{\bar{y}}}{\partial \bar{t}} = \frac{1}{B}(A^2 + B^2)\, e^{-A\bar{y}_0} \cos(\bar{t}_0 - B\bar{y}_0) \tag{2.49}$$

Now from (2.48) we see that

$$\bar{t}_0 - B\bar{y}_0 \neq \frac{\pi}{2} \text{ modulo } \pi$$

so that (2.49) would never vanish. Thus the solution for this problem also violates the Second Law for all values of the problem parameters.

Problem 4: From (2.19), (2.20) and (2.21) we have

$$\bar{u}_{\bar{y}} = \hat{u}_{0\bar{y}} + \mathcal{R}e\left\{\hat{u}_{1\bar{y}}\, e^{i\bar{t}}\right\} \tag{2.50}$$

and

$$\frac{\partial \bar{u}_{\bar{y}}}{\partial \bar{t}} = \mathcal{R}e\left\{i\, \hat{u}_{1\bar{y}}\, e^{i\bar{t}}\right\} \tag{2.51}$$

where

$$\hat{u}_{0\bar{y}} = \frac{1}{\Lambda}\bar{y} \tag{2.52}$$

and

$$\hat{u}_{1\bar{y}} = -i\frac{\psi_1}{\psi_0}\,\frac{m \sinh m\bar{y}}{\cosh m} \tag{2.53}$$

At $\bar{y} = 0$ both $\bar{u}_{\bar{y}}$ and $\partial\bar{u}_{\bar{y}}/\partial\bar{t}$ vanish so that at least on the center line the Second Law is not violated. However, there may be other $\bar{y}$'s for which the velocity gradient vanishes, but $\partial\bar{u}_{\bar{y}}/\partial\bar{t}$ does not. The answer to that question appears to be a complicated algebraic problem, but the author suspects that this flow will be found not to violate the Second Law of Thermodynamics.

3. Third-order approximation

3.1 Solutions to linearized problems

For n = 3 equation (1.6) yields

$$\underset{\sim}{T} = -p\underset{\sim}{I} + \mu \underset{\sim}{A}_1 + \mu_1^{(2)} \underset{\sim}{A}_1^2 + \mu_2^{(2)} \underset{\sim}{A}_2 + \\ + \mu_1^{(3)} (\mathrm{tr}\, \underset{\sim}{A}_1^2) \underset{\sim}{A}_1 + \mu_2^{(3)} \underset{\sim}{A}_1^3 + \mu_3^{(3)} (\mathrm{tr}\, \underset{\sim}{A}_2) \underset{\sim}{A}_1 + \\ + \mu_4^{(3)} (\underset{\sim}{A}_1 \underset{\sim}{A}_2 + \underset{\sim}{A}_2 \underset{\sim}{A}_1) + \mu_5^{(3)} \underset{\sim}{A}_3 \tag{3.1}$$

where in addition to the linear and second-order terms of (2.1) we have five new terms, each with a new material constant.

For unsteady simple shear flow the extra stress components are

$$\begin{aligned} S_{xy} &= \mu u_y + \mu_2^{(2)} u_{yt} + \bar{\mu}^{(3)} u_y^3 + \mu_5^{(3)} u_{ytt} \\ S_{xz} &= S_{yz} = 0 \\ S_{xx} &= \mu_1^{(2)} u_y^2 + 2\mu_4^{(3)} u_y u_{yt} \\ S_{yy} &= (\mu_1^{(2)} + 2\mu_2^{(2)}) u_y^2 + 2(\mu_4^{(3)} + 3\mu_5^{(3)}) u_y u_{yt} \\ S_{zz} &= 0 \end{aligned} \tag{3.2}$$

where

$$\bar{\mu}^{(3)} = 2\left(\mu_1^{(3)} + \tfrac{1}{2}\mu_2^{(3)} + \mu_3^{(3)} + \mu_4^{(3)}\right) \tag{3.3}$$

Substituting the first equation of (3.2) into (1.21) we get

$$\mu u_{yy} + \mu_2^{(2)} u_{yyt} + 3\bar{\mu}^{(3)} (u_y)^2 u_{yy} + \mu_5^{(3)} u_{yytt} = \rho u_t + \psi(t) \tag{3.4}$$

We note immediately that this governing differential equation is nonlinear and also that we now have second-order time differentiation. We present here solutions to linearized versions of the boundary value problems listed in Section 1.3.

Problem 1: Using (1.27) and (1.28) equation (3.4) reduces to

$$\bar{u}_{\bar{y}\bar{y}} + \Lambda^{(2)} \bar{u}_{\bar{y}\bar{y}\bar{t}} + 3 \Lambda_1^{(3)} (\bar{u}_{\bar{y}})^2 \bar{u}_{\bar{y}\bar{y}} + \Lambda_2^{(3)} \bar{u}_{\bar{y}\bar{y}\bar{t}\bar{t}} = \bar{u}_{\bar{t}} \tag{3.5}$$

where in addition to $\Lambda^{(2)}$ given by (2.5) we have two more dimensionless numbers

$$\Lambda_1^{(3)} = \frac{\bar{\mu}^{(3)}}{\mu} \left(\frac{U}{L}\right)^2 \qquad \Lambda_2^{(3)} = \frac{\mu \, \mu_5^{(3)}}{\rho^2 L^4} \tag{3.6}$$

Again we have the steady-state solution $(1 - \bar{y})$. Since (3.5) is non-linear we are not surprised to find that an exact solution by analysis is not readily obtained. For example, the method of separation of variables which can be used to find the solution to the linear equation (2.4) does not work in this case. We therefore settle for a perturbation analysis of the steady state solution; we assume a series solution of the form

$$\bar{u} = 1 - \bar{y} + \epsilon \, \bar{v}(\bar{y}, \bar{t}) + O(\epsilon^2) \tag{3.7}$$

where ϵ is a parameter which tends to zero. Upon substitution into (3.5) and equating coefficients of ϵ we have

$$\left(1 + 3 \Lambda_1^{(3)}\right) \bar{v}_{\bar{y}\bar{y}} + \Lambda^{(2)} \bar{v}_{\bar{y}\bar{y}\bar{t}} + \Lambda_2^{(3)} \bar{v}_{\bar{y}\bar{y}\bar{t}\bar{t}} = \bar{v}_{\bar{t}} \tag{3.8}$$

which is a linear differential equation for the first term $\bar{v}(\bar{y},\bar{t})$ in the series of (3.7). The velocity perturbation $\bar{v}$ must satisfy the boundary conditions that it vanish on both boundaries.

By separation of variables we obtain the following solution of (3.5):

$$\bar{u} = 1 - \bar{y} + \epsilon \sum_{n=1}^{\infty} \left(A_n e^{-\alpha_{1n}\bar{t}} + B_n e^{-\alpha_{2n}\bar{t}} \right) \sin n\pi \bar{y} + O(\epsilon^2) \qquad (3.9)$$

where

$$\alpha_{1n}, \alpha_{2n} = \frac{1}{2\Lambda_2^{(3)}} \left\{ \left(\frac{1}{n^2\pi^2} + \Lambda^{(2)} \right) \pm \sqrt{ \left(\frac{1}{n^2\pi^2} + \Lambda^{(2)} \right) - 4\Lambda_2^{(3)} \left(1 + 3\Lambda_1^{(3)} \right) } \right\} \qquad (3.10)$$

Because of the second-time derivative we must specify the acceleration as well as the velocity at time t = 0 in order to determine a solution.

For what combinations of values of $\Lambda^{(2)}$, $\Lambda_1^{(3)}$ and $\Lambda_2^{(3)}$ is the above solution convergent? Off hand it does not appear that the condition (2.8) for negative $\Lambda^{(2)}$ automatically carries over to the stability analysis of the third-order theory. The conditions for which the solution (3.9) and (3.10) converges or diverges are summarized in Table 1. We note that for stability $\left(\frac{1}{n^2\pi^2} + \Lambda^{(2)} \right)$, $\Lambda_2^{(3)}$ and $\left(1 + 3\Lambda_1^{(3)} \right)$ must all have the same sign. If $\bar{\mu}^{(3)}$ is negative then, by (3.6) $\left(1 + 3\Lambda_1^{(3)} \right)$ could change sign as U/ L is varied. However $\Lambda_2^{(3)}$ and $\left(\frac{1}{n^2\pi^2} + \Lambda^{(2)} \right)$ cannot change sign with U/L. Therefore in

$\frac{1}{n^2\pi^2} + \Lambda^{(2)}$	$\Lambda_2^{(3)}$	$1 + 3\Lambda_1^{(3)}$	
+	+	+	Convergent
		-	Divergent
	-	$\pm$	Divergent
-	+	$\pm$	Divergent
	-	+	Divergent
		-	Convergent

Table 1. Conditions for stability of third-order solution.

order to have stability for negative $\bar{\mu}^{(3)}$ the quantity U/ L is restricted to ranges for which $(1 + 3 \Lambda_1^{(3)})$ does not change sign. Such ranges are

$$0 < \frac{U}{L} < \sqrt{\frac{\mu}{3|\bar{\mu}^{(3)}|}} \quad \text{for} \quad 1+3\Lambda_1^{(3)} > 0 \tag{3.11}$$

or

$$\sqrt{\frac{\mu}{3|\bar{\mu}^{(3)}|}} < \frac{U}{L} \tag{3.12}$$

Problem 2: Using (1.27 and (1.31) equation (3.4) reduces to

$$\Lambda \bar{u}_{\bar{y}\bar{y}} + \Lambda^{(2)} \bar{u}_{\bar{y}\bar{y}\bar{t}} + 3\Lambda_1^{(3)} (\bar{u}_{\bar{y}})^2 \bar{u}_{\bar{y}\bar{y}} + \Lambda_2^{(3)} \bar{u}_{\bar{y}\bar{y}\bar{t}\bar{t}} = \bar{u}_{\bar{t}} \tag{3.13}$$

In addition to the dimensionless groups Λ and $\Lambda^{(2)}$ given by (2.10) and (2.5) respectively we have the two new groups

$$\Lambda_1^{(3)} = \frac{\bar{\mu}^{(3)}}{\rho L^2 \Omega} \left(\frac{U}{L}\right)^2 \qquad \Lambda_2^{(3)} = \frac{\mu_5^{(3)} \Omega}{\rho L^2} \tag{3.14}$$

For $U = 0$, and hence $\Lambda_1^{(3)} = 0$, there is no motion, after any transient motion has died out. We therefore consider small motions by assuming the following series in $\Lambda_1^{(3)}$:

$$\bar{u}(\bar{y},\bar{t}) = \Lambda_1^{(3)} \bar{v} + O[(\Lambda_1^{(3)})^2] \tag{3.15}$$

On substituting (3.15) into (3.13) and equations coefficients of $\Lambda_1^{(3)}$ we get the following linear equation for $\bar{v}$:

$$\Lambda \bar{v}_{\bar{y}\bar{y}} + \Lambda^{(2)} \bar{v}_{\bar{y}\bar{y}\bar{t}} + \Lambda_2^{(3)} \bar{v}_{\bar{y}\bar{y}\bar{t}\bar{t}} = \bar{v}_{\bar{t}} \tag{3.16}$$

The solution of (3.16) is just a slight modification of that for the corresponding solution for the second-order approximation theory; $\bar{v}$ is given by the right-hand side of (2.11) and (2.12) but (2.13) is replaced by

$$m = \left[i / (\Lambda - \Lambda_2^{(3)} + i \Lambda^{(2)}) \right]^{\frac{1}{2}} \tag{3.17}$$

Problem 3: Using (1.27) and (1.34) equation (3.4) reduces to

$$\bar{u}_{\bar{y}\bar{y}} + \Lambda^{(2)} \bar{u}_{\bar{y}\bar{y}\bar{t}} + 3 \Lambda_1^{(3)} (\bar{u}_{\bar{y}})^2 \bar{u}_{\bar{y}\bar{y}} + \Lambda_2^{(3)} \bar{u}_{\bar{y}\bar{y}\bar{t}\bar{t}} = \bar{u}_{\bar{t}} \tag{3.18}$$

where $\Lambda^{(2)}$ is given by (2.15) and $\Lambda_1^{(3)}$ and $\Lambda_2^{(3)}$ by

$$\Lambda_1^{(3)} = \frac{\bar{\mu}^{(3)} \rho \Omega U^2}{\mu^2} \qquad \Lambda_2^{(3)} = \frac{\mu_5^{(3)} \Omega^2}{\mu} \tag{3.19}$$

As in the previous problem we look for a solution for small motions by means of (3.15). The resultant linear equation for $\bar{v}(\bar{y}, \bar{t})$ is

$$\bar{v}_{\bar{y}\bar{y}} + \Lambda^{(2)} \bar{v}_{\bar{y}\bar{y}\bar{t}} + \Lambda_2^{(3)} \bar{v}_{\bar{y}\bar{y}\bar{t}\bar{t}} = \bar{v}_{\bar{t}} \tag{3.20}$$

The solution to this problem is given by the right-hand side of (2.16) with (2.17) replaced by

$$A, B = \left\{ \frac{\left[(1 - \Lambda_2^{(3)})^2 + (\Lambda^{(2)})^2 \right]^{\frac{1}{2}} \pm \Lambda^{(2)}}{2\left[(1 - \Lambda_2^{(3)})^2 + (\Lambda^{(2)})^2 \right]} \right\}^{\frac{1}{2}} \tag{3.21}$$

The parameters A and B are always real and positive regardless of the signs or magnitudes of $\Lambda^{(2)}$ and $\Lambda_2^{(3)}$.

Problem 4: Using (1.38) equation (3.4) reduces to

$$\Lambda \bar{u}_{\bar{y}\bar{y}} + \Lambda^{(2)} \bar{u}_{\bar{y}\bar{y}\bar{t}} + 3\Lambda_1^{(3)} (\bar{u}_{\bar{y}})^2 \bar{u}_{\bar{y}\bar{y}} + \Lambda_2^{(3)} \bar{u}_{\bar{y}\bar{y}\bar{t}\bar{t}} = \bar{u}_{\bar{t}} + 1 + \left(\frac{\psi_1}{\psi_0}\right)\cos\bar{t} \tag{3.22}$$

where Λ is given by (2.10) and $\Lambda^{(2)}$ by (2.5) and $\Lambda_1^{(3)}$ and $\Lambda_2^{(3)}$ are given by

$$\Lambda_1^{(3)} = \frac{\bar{\mu}^{(3)} \psi_0^2}{\rho^3 \Omega^3 L^4} \qquad \Lambda_2^{(3)} = \frac{\mu_5^{(3)} \Omega}{\rho L^2} \tag{3.23}$$

Again we look for a solution for small motions by means of (3.15). The resultant linear equation for $\bar{v}(\bar{y}, \bar{t})$ is

$$\Lambda \bar{v}_{\bar{y}\bar{y}} + \Lambda^{(2)} \bar{v}_{\bar{y}\bar{y}\bar{t}} + \Lambda_2^{(3)} \bar{v}_{\bar{y}\bar{y}\bar{t}\bar{t}} = \bar{v}_{\bar{t}} + 1 + \left(\frac{\psi_1}{\psi_0}\right)\cos\bar{t} \tag{3.24}$$

The solution to this problem is given by the right-hand side of (2.19) by (2.20) and (2.21) but (2.13) is replaced by (3.17).

3.2 Application of the Second Law

Substituting the constitutive equation (3.1) of the third-order approximation into the Second Law inequality (1.13) we find that

$$\begin{aligned} \rho\Theta\gamma = {} & \mu \operatorname{tr} \underset{\sim}{A}_1^2 + \mu_1^{(2)} \operatorname{tr} \underset{\sim}{A}_1^3 + \mu_2^{(2)} \operatorname{tr} (\underset{\sim}{A}_1 \underset{\sim}{A}_2) + \\ & + \mu_1^{(3)} (\operatorname{tr} \underset{\sim}{A}_1^2)^2 + \mu_2^{(3)} \operatorname{tr} \underset{\sim}{A}_1^4 + \mu_3^{(3)} (\operatorname{tr} \underset{\sim}{A}_2)(\operatorname{tr} \underset{\sim}{A}_1^2) + \\ & + 2\mu_4^{(3)} \operatorname{tr} (\underset{\sim}{A}_1^2 \underset{\sim}{A}_2) + \mu_5^{(3)} \operatorname{tr} (\underset{\sim}{A}_1 \underset{\sim}{A}_2) \geq 0 \end{aligned} \tag{3.25}$$

For unsteady simple shear flow (3.25) reduces to

$$\frac{1}{2}\rho\theta\gamma = \mu u_y^2 + \mu_2^{(2)} u_y u_{yt} + \bar{\mu}^{(3)} u_y^4 + \mu_5^{(3)} u_y u_{ytt} \geq 0 \tag{3.26}$$

We see from (3.26) that for steady motion we must have

$$\bar{\mu}^{(3)} \geq 0 \tag{3.27}$$

as well as (2.24).

As in Sec. 2.2 we again find by examining (3.26) that the rate of change of the velocity gradient, that is $\partial u_y/\partial t$, must be zero when the velocity gradient u_y is zero in order that (3.26) not be violated. We now investigate what this and (3.27) mean in terms of the four solutions of the previous section.

Problem 1: By (3.6) equation (3.27) implies that $\Lambda_1^{(3)}$ must be non-negative, that is

$$\Lambda_1^{(3)} \geq 0 \tag{3.28}$$

Therefore by Table 1, in order to have stability (2.8) must be satisfied and

$$\Lambda_2^{(3)} \geq 0 \tag{3.29}$$

That is we have the same condition on $\Lambda^{(2)}$ and the wave number n as we had for the second-order approximation and also the requirement that $\mu_5^{(3)}$ be positive for stability. It is interesting to note from (3.10) that perturbations for which

$$4\Lambda_2^{(3)}(1 + 3\Lambda_1^{(3)}) > \left(\frac{1}{n^2\pi^2} + \Lambda^{(2)}\right)^2 \tag{3.30}$$

decay sinusoidally rather than purely exponentially.

It likely can be shown that as in the case of the second-order approximation for this problem the velocity profile for a perturbed steady flow must be monotonic in order that the Second Law is not violated. It likely can also be shown that violation of the stability conditions also violates the Second Law.

Problems 2, 3, and 4: Since the solutions of the linearized versions of these problems differ from the solutions of the corresponding second-order problems by only unimportant changes in constants and since the Second Law criterion regarding zero velocity gradients is unchanged, all of our results of Sec. 2.2 for these problems carry over here. That is, the solutions for Problems 2 and 3 are not allowed for the third-order approximation whereas, as far as we have investigated, the solution of Problem 4 is allowed.

4. Discussion and conclusions

We have found that the Second Law of Thermodynamics in the form of the requirement that the rate of deformation work be non-negative places restrictions on allowable motions for the second and third-order approximation to fluids as well as placing restrictions on the material constants appearing in these theories.

Let us first discuss the restrictions on material constants. In addition to the classical result that the linear material coefficient μ is positive, we found from the Second Law that the third order material constants $\bar{\mu}^{(3)}$ and $\mu_5^{(3)}$ must be positive. On the other hand, we see that the sign of the second-order material constant $\mu_2^{(2)}$ which appeared in the analysis for unsteady simple shear flow, is not determined. It may be possible to find restrictions on the signs of the second-order coefficients by examining flows

other than unsteady shear. It is interesting to note that other evidence indicates that $\mu_2^{(2)}$ is non-zero and negative. Coleman and Markovitz[9] have shown that if one assumes on the "basis of thermodynamic intuition" that the stress relaxation function of linear viscoelasticity is positive for all times, then $\mu_2^{(2)}$ is negative. Furthermore, experimental determination of $\mu_2^{(2)}$, in particular by Markovitz and Brown[10], have yielded only negative values thus far.

We turn now to the restrictions placed on allowable motions. It turned out that for the oscillating wall problems, Problems 2 and 3, the solutions for the second and third-order approximation theories, were not valid for any values of the parameters of these problems. Problem 1, the problem where one wall is moving with constant velocity, only has valid solutions for restricted initial conditions: the velocity profile must be monotonic and, if $\mu_2^{(2)}$ is negative, cannot contain harmonics above a certain value which is dependent on $|\mu_2^{(2)}|$. On the other hand, the solution to Problem 4 when the flow is driven by a pulsating pressure gradient, is valid as far as we have checked. It is interesting to note in Problem 1 that the conditions for stability are consistent with satisfying the Second Law. From both stability and thermodynamic considerations, we conclude that the second and third-order theories are just approximation theories and cannot be used indiscriminately as theories for any physically well-posed problem. If such things as second-and third-order fluids existed in their own right we would expect to get valid solutions for Problems 2 and 3, and, Problem 1 for all initial conditions. On the other hand the linear theory can be used as a fluid theory in that solutions for any physically well-posed problem do not violate the Second Law. In 1951 Truesdell[11] suggested that the inequality

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9 B. D. Coleman and H. Markovitz, J. App. Phys., 35, 1 (1964).

10 H. Markovitz and D. R. Brown, Trans, Soc. Rheol., 7, 137 (1963).

11 C. Truesdell, J. Math. Pure Appl., (9), 30, 111 (1951).

(1.13) be a restriction not on constitutive equations but rather on allowable motions. Coleman in Ref. 4 advanced the point of view that (1.13) must hold for certain motions, namely those for which the reduction from (1.12) to (1.13) is valid; if (1.13) be violated in one of these motions, then the constitutive equation should be rejected. At least, the constitutive equation should be rejected for those motions for which the Second Law is violated.

It may be that the Second Law inequality (1.13) as a requirement on unsteady problems considered in this paper for the second-and-third-order fluid approximations is inconsistent with the simultaneous approximations appropriate to the thermal variables. It may be necessary to set to zero certain second and third-order thermal material constants in order to reduce to (1.13). It is intended to investigate this point in the near future.

A flow is said to be a helical flow if there exists a cylindrical coordinate system (r, θ, z) in which the physical components of the velocity have the form

$$v_r = 0 \qquad v_\theta = w(r,t) \qquad v_z = u(r,t) \tag{4.1}$$

In Ref. 5 it is developed that, for the second-order approximation, the components w and u of the velocity field are determined by two separated, linear, third-order partial differential equations. Problems corresponding to Problems 2 and 4 are then solved for in the case of Poiseuille flow $(w = 0)$ and corresponding to Problem 2 in the case of Couette flow $(u = 0)$. Explicit solutions are obtained when appropriate "small gap" approximations are made. The Second Law takes the following form for helical flow of the second-order fluid approximation:

$$\rho\theta\gamma = 2\mu\left[(r w_r)^2 + u_r^2\right] + \mu_2^{(1)}\frac{\partial}{\partial t}\left[(r w_r)^2 + u_r^2\right] \geq 0 \tag{4.2}$$

For Poiseuille flo ws (4.2) reduces to

$$\rho\theta\gamma = 2\mu u_r^2 + \mu_2^{(2)}\frac{\partial}{\partial t}(u_r^2) \geq 0 \tag{4.3}$$

and for Couette flows (4.2) reduces to

$$\rho\theta\gamma = 2\mu(r w_r)^2 + \mu_2^{(2)}\frac{\partial}{\partial t}(r w_r)^2 \geq 0 \tag{4.4}$$

It would appear that the results we have obtained from applying the Second Law to unsteady simple shear flows will carry over to the analogous problems in Poiseuille and Couette flowsof Ref. 5.

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